

## Superoxide Anion is the Intermediate in the Oxygen Reduction Reaction on Platinum Electrodes

Min-hua Shao, Ping Liu, and Radoslav R. Adzic\*

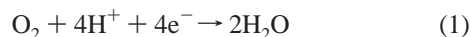
Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973

Received February 21, 2006; E-mail: adzic@bnl.gov

For over 40 years, the existence of the superoxide anion,  $O_2^-$ , as the intermediate in the oxygen reduction reaction (ORR) has been an open question in oxygen electrocatalysis, that is, over the lifetime of this area of research.<sup>1</sup> Its resolution would facilitate formulating the key step of the ORR mechanism and could profoundly affect the further development of electrocatalysts for fuel-cell cathodes. The difficulties with identifying the superoxide anion in aqueous solutions originate from a lack of adequate spectroscopic techniques and from its rapid protonation in acid solutions and disproportionation in its reaction with water.<sup>2</sup> We report here the observation of the superoxide anion in the ORR on a Pt thin film electrode captured by surface-enhanced infrared reflection absorption spectroscopy with attenuated total reflection (ATR–SEIRAS).<sup>3</sup> There are two important advantages of the ATR–SEIRAS technique in comparison with other in situ IR techniques, for example, its much higher surface sensitivity and lack of a transport limitation for reactants. Using SEIRAS with a modified experimental set up, we detected the adsorbed superoxide anion in the ORR on Pt in an aqueous solution at pH = 11.

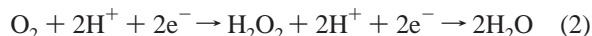
The ORR is a multielectron reaction that proceeds via several elementary steps. In aqueous solutions on Pt electrodes, it appears to occur in two pathways:

(i) A “direct” four-electron reduction, wherein four electrons are transferred in concert



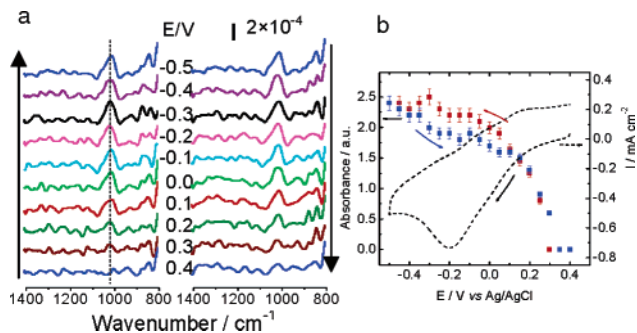
and

(ii) A “series” pathway that involves  $H_2O_2$  as the intermediate:



A series four-electron reduction involves the transfer of two electrons to form peroxide, which, without leaving the electrode’s surface, is further reduced to  $H_2O$  with the exchange of an additional two electrons and two protons. There are three possible first steps in the ORR: (i) splitting of the O–O bond upon adsorption on two Pt sites (S) in a bridge configuration,  $O_2 + 2S \rightarrow O^* + O^*$ ; (ii) formation of the superoxide anion,  $O_2 + 2S + e^- \rightarrow O_2^-$ ; and (iii) simultaneous electron and proton transfer,  $O_2 + 2S + (H^+ + e^-) \rightarrow HO_2$ . Identifying the first step would clarify the pathway of the ORR that takes place on catalytically active metal surfaces. The role of the superoxide anion and the details of the reaction mechanism on surfaces supporting a four-electron reduction pathway still defy an unquestionable description.<sup>1</sup> Such information is essential for further advances in electrocatalysis since it could resolve the question of the first reaction step on Pt—a prerequisite for formulating the reaction mechanism on a molecular level and defining the right approach for designing new electrocatalysts.

A polycrystalline Pt nanofilm, deposited chemically on a Si wafer, served as the working electrode. By placing this Si wafer



**Figure 1.** (a) SEIRAS spectra recorded for a Pt thin film electrode in  $O_2$ -saturated 0.1 M  $NaClO_4 + NaOH$  (pH 11). The reference spectrum was taken at 0.4 V before the potential sweep started. Sweep rate:  $10 \text{ mV s}^{-1}$ . (b) The potential dependence of the integrated band intensity for the O–O stretching mode of  $O_2^-$  on Pt. The ORR is shown as the dashed line.

with a Pt film on it on a hemispherical ZnSe crystal and by pressing them against the Teflon cylindrical cell body, we formed a spectroelectrochemical cell (Figure S1). This modified setup provides a good substrate for Pt and eliminates the large absorption of the Si hemisphere.<sup>4,5</sup> We confirmed its surface sensitivity by determining in situ the adsorbed formate in the oxidation of methanol. Further, by demonstrating the existence of the superoxide anion in the ORR on Pt in acetonitrile solution, we obtained another clear verification of the technique’s sensitivity and a possibility to compare the data with those obtained in aqueous solutions. It is well-known that in aprotic media  $O_2$  is reduced to  $O_2^-$  on several surfaces in a wide potential range.<sup>6–8</sup> Due to its fairly long lifetime in acetonitrile,<sup>9</sup> it was easy to detect it by the SEIRAS technique (see Figures S2 and S3).

Figure 1a shows the SEIRAS spectra observed in the ORR on Pt in  $NaClO_4$  solution at pH = 11. Buffers were not used since they usually specifically adsorb and affect the ORR. Solutions at higher pH values can attack the Si window. A band at  $1005\text{--}1016 \text{ cm}^{-1}$  appears simultaneously with the onset of the ORR at 0.2 V. Figure 1b depicts the relationship between the integrated band’s intensity and potential. This band has the same origin as that observed in aprotic solution (cf. Supporting Information), that is, the stretching mode of the O–O bond of adsorbed  $O_2^-$ . In addition, the potential dependence of this band (easily seen in Figure S4) indicates that it comes from an adsorbed species rather than from the solution phase species. As expected, in  $N_2$ -saturated solution, the IR spectra are featureless in the range of  $1200\text{--}1000 \text{ cm}^{-1}$ . In 0.1 M  $HClO_4$  solution (pH = 1), no band is observed, probably due to the much shorter lifetime of  $O_2^-$  in acid solution because of its rapid protonation at low pH values.<sup>2,8</sup>

The stretching mode of adsorbed  $O_2^-$  and  $O_2^{2-}$  on metals and their oxides in the gas phase have been observed at  $1015\text{--}1180^{10\text{--}13}$  and  $640\text{--}900 \text{ cm}^{-1,10\text{--}12,14}$  respectively. However, for molecular oxygen on a Pt(111) surface, the assignments of the observed bands are controversial. Thus, the band at  $860\text{--}880 \text{ cm}^{-1}$  was assigned

to the bridge-bonded peroxide<sup>14–17</sup> or superoxide,<sup>18</sup> and the lower frequency one (690–700 cm<sup>-1</sup>) was to peroxide<sup>15,17</sup> or the peroxy species adsorbed on surface defects.<sup>16</sup> Wang and Andrews assigned the band at 930 cm<sup>-1</sup> observed on Pt in isolated matrix to superoxide.<sup>19</sup> The frequency (1005–1016 cm<sup>-1</sup>) of the band we observed is higher than those detected in the gas phase. This difference may be caused by the effect of the solvent. Compared with the frequency of O<sub>2</sub><sup>-</sup> on Au in the gas phase (1046 cm<sup>-1</sup>),<sup>20</sup> the band for HO<sub>2</sub> reported by Li and Gewirth for acid solution is 120 cm<sup>-1</sup> higher (1165 cm<sup>-1</sup>).<sup>21</sup> The solvent may have similar effects on Pt surfaces. It was established that in the gas phase the frequency of the perturbed O–O stretching is 100–200 cm<sup>-1</sup> higher than that of an unperturbed one.<sup>10,22</sup>

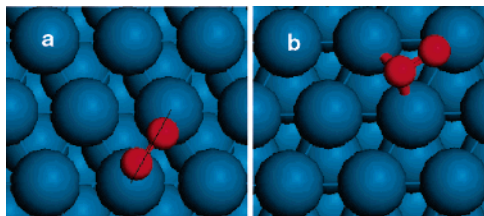
There are several reports on the detection of the superoxide anion in electrochemical systems. These were atypical systems, and the results are difficult to relate to the key question of the superoxide existence in the ORR in common situations, including the ORR at fuel-cell cathodes.<sup>2,21,23</sup>

To further understand the adsorption of O<sub>2</sub><sup>-</sup> on Pt surfaces, density functional theory (DFT) calculations were undertaken to determine the structure and vibrational frequency for its adsorption on Pt(111) (Table 1). The binding energy ( $E_b$ ), the bond length of

**Table 1.** Calculated Parameters for Free O<sub>2</sub><sup>-</sup> Molecule and Adsorbed O<sub>2</sub><sup>-</sup> on Pt(111) at Different Coverages

O <sub>2</sub> <sup>-</sup>	ML	$E_b$ (eV)	$d_{O-O}$ (Å)	site	$\nu_{O-O}$ (cm <sup>-1</sup> )
O <sub>2</sub> <sup>-</sup> /Pt(111)			1.37		1123
	1/9	-0.60	1.39	b-fcc-t	796
	1/9	-0.76	1.37	t-b-t	875
	1/4	-0.68	1.36	t-b-t	896
	1/2	-0.39	1.34	t-b-t	1051
1	>0	1.27		1292	

O–O ( $d_{O-O}$ ), and the frequency of O–O stretching ( $\nu_{O-O}$ ) all vary with increasing coverage. In accordance with the previous study,<sup>24</sup> our DFT calculations show that, at low coverage of 1/9 ML, the O<sub>2</sub><sup>-</sup> adsorption at the t–b–t (Figure 2a) sites of Pt(111) is the most



**Figure 2.** Optimized geometries for the adsorption of O<sub>2</sub><sup>-</sup> (a) t–b–t and (b) b–fcc–t sites of Pt(111) (small red, O; big blue, Pt).

stable ( $E_b = -0.76$  eV) followed by that at the t–fcc–b sites ( $E_b = -0.60$  eV; Figure 2). Compared to the free O<sub>2</sub><sup>-</sup> molecule, the O–O bond length hardly changes when adsorbed at the t–b–t sites of Pt(111) ( $d_{O-O} = 1.37$  Å). Increasing the coverage to 1/4 ML, the t–b–t site again is the preferred one, with  $E_b$  and  $d_{O-O}$  changed slightly. A dramatic change takes place at coverage of 1/2 ML when the O<sub>2</sub><sup>-</sup>–O<sub>2</sub><sup>-</sup> repulsion becomes effective. Although the t–b–t site still is favored, the binding energy between O<sub>2</sub><sup>-</sup> and Pt(111) weakens ( $E_b = -0.39$  eV), and the O–O bond shrinks further to 1.34 Å. Consequently, we observe a big shift of  $\nu_{O-O}$  to the frequency region around 1000 cm<sup>-1</sup>. Increasing the coverage to 1 ML results in desorption of O<sub>2</sub><sup>-</sup> from the surface. The bridge-bonded O<sub>2</sub> to Pt surfaces yielded in the above calculations agrees with the experimental data<sup>25</sup> and the results of two theoretical calculations of the reaction pathways on the ORR.<sup>26,27</sup>

The spectral and voltammetry data in Figure 1 and the results of the DFT calculations led us to conclude that the ORR on Pt in aqueous solutions involves the formation of O<sub>2</sub><sup>-</sup> as the first reaction step. This conclusion is supported by a lack of spectra and of reduction current at the potentials where the ORR does not occur and in N<sub>2</sub>-saturated solutions, and by the spectra we obtained for the superoxide anion in O<sub>2</sub> reduction on Pt in acetonitrile solutions. An additional support for this finding, although not uniquely specific, is the intrinsic Tafel slope for this reaction of -120 mV<sup>28</sup> that is a criterion for the first charge transfer slow step. Proving the existence of the superoxide anion resolves the question of the reaction pathway in the ORR on Pt, which can considerably simplify the molecular formulation of the reaction mechanism. On the basis of the finding of the O<sub>2</sub><sup>-</sup>, we can conclude that the series reaction pathway, given by eq 2, is operative for the ORR on Pt electrodes in alkaline solutions. There is no fundamental reason it should not be operative in acid solutions. In addition, this finding resolves the dilemma in the theoretical treatment of the ORR kinetics<sup>29</sup> and provides basic information for designing new electrocatalysts.

**Acknowledgment.** This work is supported by U.S. Department of Energy, Divisions of Chemical and Material Sciences, under the Contract No. DE-AC02-98CH10886. M.-H.S. acknowledges partial support from Department of Materials Science and Engineering, State University of New York at Stony Brook.

**Supporting Information Available:** Experimental procedures and supporting figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Adzic, R. R. In *Electrocatalysis*; Lipkowsky, J., Ross, P. N., Eds.; Wiley: New York, 1998.
- Yeager, E. *Electrochim. Acta* **1984**, *29*, 1527.
- Chen, Y. X.; Miki, A.; Ye, S.; Sakai, H.; Osawa, M. *J. Am. Chem. Soc.* **2003**, *125*, 3680.
- Martin, H. B.; Morrison, P. W., Jr. *Electrochem. Solid-State Lett.* **2001**, *4*, E17.
- Shao, M. H.; Adzic, R. R. *J. Phys. Chem. B* **2005**, *109*, 16563.
- Maricle, D. L.; Hodgson, W. G. *Anal. Chem.* **1965**, *37*, 1562.
- Sawyer, D. T.; Chlericato, G. J.; Angells, C. T.; Nannl, E. J. J.; Tsuchlya, T. *Anal. Chem.* **1982**, *54*, 1720.
- Sawyer, D. T.; Seo, E. T. *Inorg. Chem.* **1977**, *16*, 499.
- Vasudevan, D.; Wendt, H. J. *Electroanal. Chem.* **1995**, *192*, 69.
- Chen, M.; Tench, A. J. In *Advances in Catalysis*; Eley, D. D., Pines, H., Weisz, P. B., Eds.; Academic Press: New York, 1983; Vol. 32, p. 2.
- Eickmans, J.; Goldmann, A.; Otto, A. *Surf. Sci.* **1983**, *127*, 153.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; John Wiley & Sons: New York, 1997.
- Li, C.; Domen, K.; Maruya, K.-I.; Onishi, T. *J. Am. Chem. Soc.* **1989**, *111*, 7683.
- Sexton, B. A. *Appl. Phys. A* **1981**, *26*, 1.
- Avery, N. R. *Chem. Phys. Lett.* **1983**, *96*, 371.
- Gland, J. L.; Sexton, B. A.; Fischer, G. B. *Surf. Sci.* **1980**, *95*, 587.
- Steininger, H.; Lehwald, S.; Ibach, H. *Surf. Sci.* **1982**, *123*, 1.
- Outka, D. A.; Stohr, J.; Jark, W. *Phys. Rev. B* **1987**, *35*, 4119.
- Wang, X. F.; Andrews, L. J. *J. Phys. Chem. A* **2001**, *105*, 5815.
- Itoh, T.; Abe, K.; Dokko, K.; Mohamedi, M.; Uchida, I.; Kasuya, A. *J. Electrochem. Soc.* **2004**, *151*, A2042.
- Li, X.; Gewirth, A. A. *J. Am. Chem. Soc.* **2005**, *127*, 5252.
- Lu, X. Y.; Faguy, P. W.; Liu, M. L. *J. Electrochem. Soc.* **2002**, *149*, A1293.
- Forman, H. J.; Fridovich, I. *Science* **1972**, *175*, 339.
- Eichler, A.; Hafner, J. *Phys. Rev. Lett.* **1997**, *79*, 4481.
- Adzic, R. R.; Wang, J. X. *J. Phys. Chem. B* **1998**, *102*, 8988.
- Panchenko, A.; Koper, M. T. M.; Shubina, T. E.; Mitchell, S. J.; Roduner, E. *J. Electrochem. Soc.* **2004**, *151*, A2016.
- Sidik, R. A.; Anderson, A. B. *J. Electroanal. Chem.* **2002**, *528*, 69.
- Wang, J. X.; Markovic, N. M.; Adzic, R. R. *J. Phys. Chem. B* **2004**, *108*, 4127.
- Nørskov, J. K.; Rossmeisl, J.; Lindqvist, A. L. L.; Kitchin, J. R.; Bligaard, T.; Jönsson, H. *J. Phys. Chem. B* **2004**, *108*, 17886.

JA061246S